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(54) PHOTOVOLTAIC CELLS

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Description

The invention relates to photovoltaic cells. Transition metal dyestuffs are coated on titanium dioxide films rendering the device effective in the conversion of visible light to electric energy.

Titanium dioxide films (layers) are known for their semiconductive properties and this property renders them useful for photovoltaic cells. However titanium dioxide has a large band gap and therefore it does not absorb light in the visible region of the spectrum. For solar applications it is important that the titanium dioxide film be coated with a photosensitiser which harvests light in the wavelength domain where the sun emits light, i.e. between 300 and 2000 nm. Thermodynamic considerations show that conversion of solar energy into electricity is achieved in the most efficient fashion when all the emitted photons with wavelengths below 820 nm are absorbed by the photosensitizer. The optimal dye for solar conversion should therefore have an absorption onset around 800nm and the absorption spectrum should be such that it covers the whole visible domain.

A second requirement for efficient solar light energy conversion is that the dyestuff after having absorbed light and thereby acquired an energy-rich state is able to inject with practically unit quantum yield, an electron in the conduction band of the titanium dioxide film. This requires that the dyestuff is attached to the surface of the titanium dioxide through suitable interlocking groups. The function of the interlocking group is to provide electronic coupling between the chromophoric group of the dyestuff and the conduction band of the semiconductor. This type of electronic coupling is required to facilitate electron transfer between the excited state of the dyestuff and the conduction band. Suitable interlocking groups are π-conducting substituents such carboxylate groups, cyano groups, phosphate groups or chelating groups with π-conducting character such as oximes, dioximes, hydroxy quinolines, salicylates and alpha keto enolates. The electrons, photoinjected by the dyestuff, generate electrical current in the external circuit when the photovoltaic cell is operated.

U.S. Patent No. 4,117,210 describes a photovoltaic cell comprising a light transmitting electrically conductive layer, which functions as an electrode, deposited on a glass plate. A semiconductor metal oxide thin film, such as a titanium dioxide film, is subsequently deposited onto this electrode. A semi transparent metal film, such as a thin film of titanium constitutes an intermediate layer between said metal oxide film and said electrode, in order to facilitate electron transfer between them.

Such photovoltaic cell harvests only UV light due to the large band gap of the oxide semiconductors employed.

European Patent Application No. 0333641 discloses a photovoltaic cell comprising an electrically conductive first plate to which a thin film of a polycrystalline semiconductor oxide, such as titanium oxide, coated with a transition metal complex photosensitizer, is deposited. A conductive and light transmitting second plate with no semiconductor oxide coating is separated from the first plate by a thin electrolyte layer.

According to the invention there is provided a solar-light-responsive photovoltaic cell comprising a first electrode including:

i) a light transmitting electrically conductive layer deposited on a glass plate or a transparent polymer sheet;

ii) at least one porous high surface area titanium dioxide layer applied to said light transmitting electrically conductive layer;

iii) a dopant applied to at least the outermost titanium dioxide layer, said dopant being selected from a divalent metal ion, trivalent metal ion and boron; and

iv) a photosensitizer applied to the dopant-containing TiO_2 layer, said photosensitizer being attached to the TiO_2 layer by means of interlocking groups, said interlocking groups being selected from carboxylate groups, cyano groups, phosphate groups and chelating groups with π- conducting character selected from oximes, dioximes, hydroxy quinolines, salicylates and α-keto-enolates.

Still further according to an embodiment of the invention there is provided a solar-light-responsive photovoltaic cell further comprising:

i) a second electrode, at least one of the first and second electrodes being transparent and having a visible light transmittance of at least 60%, the electrodes being arranged so as to define a receptacle between them, in which receptacle an electrolyte containing a redox system is located, and

ii) means for permitting the output of an electrical current generated by the cell;

wherein the improvement comprises the electrolyte-contacting surface of said film being doped with at least one ion selected from divalent and trivalent metals and boron.

For the purposes of this invention it is essential that the dopant be confined to the surface of the titanium dioxide, that is, to the titanium dioxide/electrolyte interface or very close thereto. The preferred way of achieving this is by the application of a series of layers of titanium dioxide casting, one on top of the other, with up to the last three layers containing the dopant. Preferably, the last four layers further to the outermost layer contain the dopant.

The photosensitiser dye applied to the doped TiO_2 layer is preferably a ruthenium, osmium or iron complex or a combination of two or three transition metals in one supramolecular complex.

A photovoltaic cell according to the invention as defined in claim 3 comprises:

i) an electrically conductive first plate on which a multilayer TiO_2 film having a thickness of 0.1-50 μm is coated, said TiO_2 film being coated with a transition metal complex photosensitizer attached to the TiO_2 layer by means of interlocking groups, said interlocking groups being selected from carboxylate groups, cyano groups, phosphate groups and chelating groups with π- conducting character selected from oximes, dioximes, hydroxy quinolines, salicylates and α-keto-enolates, at least the outermost layer of the TiO_2 film being doped with a dopant selected from a divalent metal ion, trivalent metal ion and boron,

ii) and a conductive second plate separated from the first plate by a thin layer of electrolyte (3), whereby the visible light transmittance of at least one of the plates is at least 60% and only the first plate has a TiO_2 coating.

The second plate (also known as "the counterelectrode") may be coated with a thin layer (preferably up to 10 microns thickness) of an electrocatalyst. The role of the electrocatalyst is to facilitate the transfer of electrons from the counterelectrode to the electrolyte. A further possible modification of the counterelectrode is to make it reflective to the light that impinges thereon, having first passed through the electrolyte and the first plate.

The photosensitiser applied to the surface of the titanium dioxide is preferably selected from a ruthenium, osmium, or iron transition metal complex or combinations thereof.

Preferably the electrolyte contains a redox system (charge transfer relay). Preferably such systems include iodine/iodide solutions, bromine/bromide solutions, hydroquinone solutions or solutions of transition metal complexes transferring a nonbonding electron. The charge transfer relays present in the electrolyte transport electric charge from one electrode to the other. They act as pure mediators and undergo no chemical alteration during the operation of the cell. It is preferable that the electrolytes in a photovoltaic cell according to the invention are dissolved in an organic medium so that the dyes applied to the titanium dioxide surface are insoluble therein. This has the advantage that the cell has a long-term stability.

Preferred organic solvents for the electrolyte include but are not limited to water, alcohols and mixtures thereof, non-volatile solvents such as propylene carbonate, ethylene carbonate and methyl pyrrolidinone, mixtures of non-volatile solvents with viscosity reducing solvents such as acetonitrile, ethylacetate or tetrahydrofuran. Additional solvents are dimethylsulfoxide or dichloroethane. Where miscible, mixtures of any of the above may be used.

Preferably the titanium dioxide films have a roughness factor greater than one, the roughness factor being defined as the ratio of true to apparent surface area. More preferably the roughness factor is 10-1000, most preferably 50-200. Preferably the titanium dioxide layers are built up on the surface of the conductive layer using the on of two methods. One, the sol-gel method is described in "Stalder and Augustynski, J. Electrochem. Soc. 1979, 126:2007" and in Example 35. The other, the "colloidal method" is described in Examples 35 and 37.

The glass or polymer plate which is used for the transparent plate of the cell according to the invention is any transparent glass or polymer onto which a light transmitting electrically conductive layer has been deposited, such that the plate preferably has a visible light transmittance of 60-99%, more preferably 85-95%. Preferably the transparent conductive layer has a surface resistance of less than 10 ohms per square cms, preferably from 1 to 10 ohms per square cm. Preferably the transparent conductive layer used in a photovoltaic cell according to the invention is made of tin dioxide doped with ca. 0.8 atom percent of fluorine and this layer is deposited on a transparent substrate made of low-cost soda lime float glass. This type of conducting glass can be obtained from Asahi Glass Company, Ltd. Tokyo, Japan. under the brand name of TCO glass. The transparent conductive layer can also be made of indium oxide doped with up to 5% tin oxide, deposited on a glass substrate. This is available from Balzers under the brand name of ITO glass.

A photovoltaic cell according to the invention has the following advantages when compared to existing cells.

1. It has a higher open circuit voltage than conventional cells while maintaining a fill factor comparable to that of conventional solar cells. The fill factor is defined as the electrical power output at the optimal cell voltage for light energy conversion divided by the product of open circuit voltage and short circuit current. A high open circuit voltage is very important for practical applications since it allows to operate the cell at lower Ohmic losses than conventional photovoltaic cells which have a smaller open circuit voltage.

2. In contrast to p-n junction solid state solar cells where the semiconductor assumes the function of light absorption and carrier transport simultaneously, a photovoltaic cell according to the invention achieves the separation of these functions. Light is absorbed by the very thin layer of dyestuff adsorbed onto the surface of the titanium dioxide film while the charge carrier transport is carried out by the titanium dioxide

film. As a consequence, a photovoltaic cell according to the present invention operates as a majority carrier device. This has the advantage that imperfections such as grain boundaries or other types of crystalline disorders or impurities and disorder within the TiO_2 film do not decrease the efficiency of the cell as would be the case if minority carriers were involved in the cell operation. Conventional solar cells operate with minority charge carriers and this explains the need to fabricate these cells from highly pure and ordered materials which are costly. The present invention permits the development of cheap solar cells. All the materials employed in the present cells are inexpensive, apart from the sensitiser. However, the latter is used in such small quantities, typically 0.3 millimoles per square meter, that its cost can be neglected with respect to that of the other components, e.g. the glass plates.

3. A further consequence of the fact that the present cell operates as a majority carrier device is that the cell voltage depends to a smaller degree on the intensity of the impinging light than that of a conventional solar cell. Thus, the present cell maintains its high efficiency under diffuse light or in cloudy weather, while the efficiency of a conventional cell decreases sharply under these conditions.

4. By selecting appropriate dyestuffs, the cell can be optimised with respect to solar energy conversion. A photovoltaic cell according to the present invention has an optimal threshold wavelength for light absorption at 820 nm corresponding to an energy of 1,5 eV. Such a cell can attain higher solar conversion efficiencies than a cell based on silicon.

5. A photovoltaic cell according to the present invention is able to convert diffuse light more efficiently to electricity than systems previously known.

6. A further advantage of a preferred photovoltaic cell according to the present invention is that it can be irradiated from the front side, back side, or both sides. It can be irradiated by passing the light through the counter-electrode and the electrolyte to the dyestuff absorbed at the TiO_2 layer or through the TiO_2 layer to the absorbed dyestuff. If both the dye coated electrode and the counterelectrode are transparent, then light from all directions can be collected. In this way it is possible, in addition to direct sunlight, to harvest diffuse reflected light. This will improve the overall efficiency of the solar cell.

7. A further advantage of a photovoltaic cell according to the present invention is that the specific texture and electronic properties of the dye loaded TiO_2 layer allow the counterelectrode to be placed directly on top of the working electrode. In other words, there is no need to employ a spacer such as a polymer membrane to keep the two electrodes apart in order to avoid the formation of a short circuit. The dielectric features of the dye coated TiO_2 layer are such that even though it may be in direct contact with the counter-electrode there is no break-through current due to short circuiting of the two electrodes. This is an important advantage for practical application of the cell since it simplifies the construction of the device and reduces its cost.

In the sol gel method it is preferable that only the last three, the last two or just the very top layer of the titanium dioxide is doped with a divalent or trivalent metal in an amount of not more than 15% doping by weight. However, the deposition of the pure dopant in form of a very thin top oxide layer can also be advantageous. In the latter case, a blocking layer is formed which impedes leakage current at the semiconductor- electrolyte junction. All of the TiO_2 layers are formed by the sol gel process method described in Example 34. Preferably the number of TiO_2 layers deposited is 10-11. Preferably the total thickness of the TiO_2 film is from 5 to 50 microns (more preferably 10-20 microns).

The photosensitising layer may be produced by applying to the TiO_2 layer a dye defined below.

Accordingly, a new series of dyes has been developed to act as efficient photo-sensitizers.

The photosensitizing dye comprises a transition metal (preferably ruthenium, osmium or iron) complex, the ligands being bidentate or tridentate or polydentate polypyridyl compounds, which may be unsubstituted or substituted. Preferably one or more of these pyridyl compounds contains at least one cyano group.

Still further, there is provided a photosensitizing dye, comprising a transition metal (preferably ruthenium, osmium, or iron) complex, at least one ligand comprising a mononuclear, cyano-containing pyridyl compound.

Preferably, there are three ruthenium atoms and six donating atoms per complex in the photosensitising dye.

According to an embodiment of the invention, there is provided compounds of the formulas 1 to 10:

$$[M(L^a)(L^b)\,(\mu\text{-}(NC)M(CN)(L^c)(L^d))_2] \qquad (1)$$

$$[M(L^a)(L^b)\,(\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN)M(CN)(L^c)(L^d))_2] \qquad (2)$$

$$[M(L^a)(L^b)\,(\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN))_2M(L^c)(L^d)] \qquad (3)$$

$$[(L^a)(L^b)(X)M\ \mu\text{-}(NC)M(CN)(L^c)(L^d)] \qquad (4)$$

$$[M(L^a)(L^b)(X)_2] \qquad (5)$$

$$[M(L^a)(L^b)(L^c)] \qquad (6)$$

$$[M(L^a)(L^b)\,(\mu\text{-}(NC)M(L^c)(L^g))_2] \qquad (7)$$

$$[M(L^a)(L^b)\,(\mu\text{-}(NC)M(L^c)(L^d)\ \mu\text{-}(CN)M(L^c)(L^g))_2] \qquad (8)$$

$$[M(L^a)(L^g)\ \mu\text{-}(NC)M(L^g)(L^b)] \quad (9)$$

$$[M(L^a)(L^g)(X)] \quad (10)$$

in which each M is independently selected from ruthenium, osmium, or iron; μ-(CN) or μ-(NC) indicates that the cyano group bridges two metal atoms;

each L^a, L^b, L^c and L^d independently is selected from 2,2'-bipyridyl, unsubstituted or substituted by one or two COOH groups; 2,2'bipyridyl substituted by one or two groups selected from C_{1-16} alkyl, C_{1-16} alkoxy and diphenyl; 2,2'-biquinoline unsubstituted or substituted by one or two carboxy groups; phenanthroline, unsubstituted or substituted by one or two carboxy groups and /or one or two hydroxy groups, and/or one or two oxime groups; 4,7 diphenyl-1, 10-phenanthroline disulfonic acid;diazatriphenylene, diaza-hydroxycarboxyl-triphenylene (for example 1,12 diazatriphenylene or 1,12 diaza (6-hydroxy-7-carboxy)triphenylene); carboxy pyridine - (for example 2-carboxypyridine);phenyl pyridine; 2,2'-Bis(diphenylphosphino) 1,1'- binaphthalene; (pyridyl azo) resorcinol (for example 4-(2-pyridyl(azo)resorcinol); bis (2-pyridyl) C_{1-4} alkane; N,N,N',N'-tetra C_{1-4} alkyl ethylene diamine;and di-C_{1-4} alkyl glyoxime; 2,2'-biimidazole; 2,2'-bibenzimidazole; 2,-(2'-pyridyl)-N-methylbenzimidazole; 2,-(2'-pyridyl)benzothiozole; 2,-(2'-pyridylmethyl)benzimidazole;

L^g is selected from terpyridyl, (unsubstituted or substituted by phenyl, which phenyl group is unsubstituted or substituted by COOH)(for example 2,2',6',2" terpyridine) and dicarboxy-pyridine (preferably 2,6-dicarboxy-pyridine); 2,6-bis(benzimidazole-2'-yl) pyridine; 2,6-bis(N-methylbenzimidazole-2'-yl)pyridine; 2,6-bis (benzothiazol-2'-yl)pyridine.

each X independently is halide, H_2O, CN^-, NCS^-, amine (primary or preferably secondary alkylamine) and/or pyridine.

Preferably, one of L^a and L^b has an interlocking group selected as defined above, preferably a -COOH and/or an OH and/or an =N-OH and/or -CO-NH_2 group.

Preferably, the terpyridyl when substituted is substituted by C_{1-4} alkyl (preferably methyl) and/or C_{1-16} alkoxy (preferably methoxy) and/or carboxy on one or more of the pyridyl groups - for example 2,2',6',2" terpyridine.

Preferably any phenanthroline in a L^a to L^d is selected from 5-carboxy-6-hydroxy-1,10-phenanthroline and 5,6-dioxime-1,10-phenanthroline.

Preferably any diaza hydroxy carboxyl triphenylene in L^a to L^d is 1,12-diaza-6-hydroxy-7-carboxyl triphenylene.

Preferably any C_{1-16} alkyl -2,2' bipyridyl in L^a to L^d is 4- C_{1-16} alkyl -2,2' bipyridyl.

Preferably any carboxy pyridine in L^a to L^d is 2-carboxypyridine.

Preferably any (pyridyl azo) resorcinol in L^a to L^d, is 4-(2-pyridyl azo) resorcinol.

The photosensitiser dyes can be used in photovoltaic cells.

Compounds of formula 1

$$[M(L^a)(L^b)[\mu\text{-}(NC)M(CN)(L^c)(L^d)]_2] \quad (1)$$

can be prepared by reacting one mole of a compound of formula 1a

$$M(L^a)(L^b)\ Cl_2 \quad (1a)$$

with 2 moles of a compound of formula 1b

$$M(L^c)(L^d)(CN)_2 \quad (1b)$$

at an elevated temperature.

Compounds of formula 2 can be prepared by reacting one mole of a compound of formula 1 with a slight excess of two moles of a compound of formula 2a

$$[M(L^c)(L^d)(CN)(H_2O)] \quad (2a)$$

at an elevated temperature.

Compounds of formula 3 can be prepared by reacting a compound of formula 1a defined above with 1 mole of a compound of formula 3a

$$((NC)M(L^c)(L^d)(CN))_2M(L^c)(L^d) \quad (3a)$$

at an elevated temperature.

Compounds of formula 4 can be prepared by reacting one mole of a compound of formula 4a

$$M(L^a)(L^b)(X)_2 \quad (4a)$$

with one mole of a compound of formula 4b

$$M(L^c)(L^d)(CN)2 \quad (4b).$$

Compounds of formula 5 can be prepared by reacting one mole of a compound of formula 5a

$$MX_3 \quad (5a)$$

with one mole of L^a and one mole of ligand forming compound L^b at an elevated temperature.

Compounds of formula 6 can be prepared by reacting one mole of a compound of formula 6a

$$M(L^a)(L^b)Cl_2 \quad (6a)$$

with excess of one mole of a ligand forming compound L^c at an elevated temperature.

Compounds of formula 7 can be prepared by reacting one mole of a compound of formula 7a

$$M(L^a)(L^b)Cl_2 \qquad (7a)$$

with 2 moles of a compound of formula 7b

$$CN\ M\ (L^c)(L^g) \qquad (7b)$$

at an elevated temperature.

Compounds of formula 8 can be prepared by reacting a compound of formula 8a

$$M(L^a)(L^b)Cl_2 \qquad (8a)$$

with two moles of a compound of formula 8b

$$CN\ M(L^c)(L^d)CN\ M(L^c)(L^g) \qquad (8b).$$

Compounds of formula 9 can be prepared by reacting a compound of formula 9a

$$M(L^a)(L^g)(H_2O) \qquad (9a)$$

with one mole of a compound of formula 9b

$$M(L^b)(L^g)(CN) \qquad (9b)$$

at an elevated temperature.

Compounds of formula 10 can be prepared by reacting one mole of a compound of formula 10c

$$M(L^g)(X)_2\ Cl \qquad (10c)$$

with one mole of ligand forming compound L^a at an elevated temperature.

Further, in a photovoltaic cell according to the invention there may be provided an electrode comprising a transparent TiO_2 layer on a glass support, for use in photovoltaic cell systems.

Preferably, such a clear layer is produced by dispersion of collidal TiO_2 solutions on a glass support. Preferably, such solutions are prepared by hydrolysis of $Ti(OCH(CH_3)_2)_4$.

By the term "transparent" is meant that 70%, more preferably 80%, of incident light passes through the glass.

Photosensitizer dyes which can be used in the photovoltaic cells of the invention will now be illustrated by the following Examples 1-33.

Example 1

The ligands 2,2' bipyridine, 4,4'-COOH 2,2'-bipyridine and $RuCl_3\ 3H_2O$ are commercial samples from Alfa and Fluka. All other materials are reagent grade and are used without further purification. Cis-dichloro bis (4,4'-COOH-2,2-bipyridine)Ru(II) is known.

a) Synthesis of cis-dicyano bis (2,2'-bipyridine)Ru(II) (- relating to compounds of formula 5 above)

800 mg (1.45 mmol) of cis-dichloro bis (2,2'bipyridine) is dissolved in 80 ml of DMF, under N_2 in the dark. To this solution 190 mg (2.91 mmol) of KCN which is separately dissolved in H_2O are added. The solution is heated at reflux for 3 hours. During the course of reaction, the dark purple solution changes to an orange red. The progress of this reaction is monitored with the help of UV/vis Spectrophotometer. The solution is filtered through a fine, glass frit and the filtrate is evaporated under reduced pressure, to dryness. The residue is dissolved in 20 ml of H_2O and filtered, in order to remove any unreacted staring complex. Again the filtrate is evaporated to dryness. The resulted residue is dissolved in 15 ml of ethanol, and filtered through a fine glass frit, which removes quantitatively the product KCl. To the filtrate, 150 ml of diethylether is added. The turbid solution is placed in a refrigerator for 2 hours, after which time the precipitate is collected by filtration on to a glass frit. The precipitate is washed with 3 x 5 ml portions of 2:10 ethanol diethylether mixture, followed by anhydrous diethylether, and dried in vacuo; yield 0.62 gr, 90%. The purity of this complex can be checked by elemental analysis and luminescence behavior.

b) Synthesis of cis-dicyano bis (4,4'-COOH-2,2'-bipyridine) Ru(II) (- relating to compounds of formula 5 above)

This complex is prepared as described by a method analogous to that previously described except for the isolation and purification steps. After refluxing the reactants cis-$[Ru(4,4'\text{-}COOH\text{-}2,2'\text{-}bpy)_2Cl_2]$ and KCN in 1:2 ratio for 4 hours, the solution is allowed to cool and filtered through a fine glass frit. The filtrate is evaporated to dryness, under reduced pressure. The resulting residue is dissolved in H_2O at pH 6-7 and the required complex is isolated as a neutral salt at its isoelectric point, pH 2.6.

c) Synthesis of cyanobridged trimers of Ru (II); $[RuL_2[(NC)_2RuL_2']_2]$ (- relating to compounds of formula 1 above)

A complex as shown in Table 1 below can be prepared as follows. 307 mg (0.43 mmol) of RuL_2Cl_2 is dissolved in 30 prepared of alkaline DMF, under N_2, in the dark. To this solution 400 mg (0.86 mmol) of $RuL_2'(CN)_2$ is added. The solution is heated at reflux for 6 hours and allowed to cool to room temperature. The solution is filtered through a fine glass frit and the filtrate is evaporated to dryness. The resulted re-

sidue is dissolved in H_2O at pH 6-7. The pH of this solution is lowered to 3.2, which results in a dense precipitate. The solution is placed in a refrigerator for 10 hours, after which time the precipitate is collected by filtration onto a glass frit. The precipitate is washed with 2:5 acetone diethylether mixture followed by anhydrous diethylether and dried in vacuo; yield 450 mg (69%).

Example 2 (- relating to compounds of formula 1 above)

Example 1c is repeated using 0.86 mmol of $Ru(II)L_2(CN)_2$ to produce a compound defined in Example 2 in Table 1

Example 3 to 8

By a method according to Example 1 complexes as defined in Table 1 below can be prepared from appropriate reactants.

Table 1

	Complex	L	L'
1	$[Ru(L_2\{(CN)_2Ru(L')_2\}_2]$	$4,4'-(COOH)_2bpy$	2,2'-bpy
2	$[Ru(L_2\{(CN)_2Ru(L)_2\}_2]$	$4,4'-(COOH)_2bpy$	
3	$[Ru(L_2\{(CN)_2Ru(L')_2\}_2]$	$4,4'-(COOH)_2bpy$	$4,4'-(Me)_2$-bpy
4	$[Ru(L_2\{(CN)_2Ru(L')_2\}_2]$	$4,4'-(COOH)_2bpy$	$4,4'-(ph)_2$-bpy
5	$[Ru(L_2\{(CN)_2Os(L')_2\}_2]$	$4,4'-(COOH)_2bpy$	2,2'-bpy
6	$RuL_2(CN)_2$	$4,4'(COOH)_2bpy$	
7	$RuL_2(CN)_2$	2,2'-bpy	
8	$RuL_2(CN)_2$	$4,4'-(Me)_2bpy$	

in which
"bpy" = 2,2' - bipyridyl
"Me" = methyl
"ph" = phenyl

Examples 9-33

By a method analogous to that of Example 1, complexes as defined in Table 2 can be prepared from suitable reactants.

In Table 2, bpy = 2,2' bipyridyl; biq = 2,2' biquinoline and phen = 1,10 phenanthroline
in example 19 2-phenylpyridine is used
in example 22 straight and branched alkyl groups are used
in example 26 N,N-tetramethyl and C,C - tetramethyl ethylene diamine are used
in example 27 2,2' bis(diphenylphosphino)-1,1'binaphthylene is used
in examples 28,30 and 33 1,10 orthophenanthrolene is used and
in example 31 4-(2-pyridyl) azo resorcinol is used

Table 2

List od Ru-complexes with one or more 4,4'-dicarboxy-2,2'-bipyridine ligands

#	Complex	L	L'
9	[RuL_3]	4,4',5,5'-$(COOH)_4$-2,2'-bpy	-
10	[RuL_3]	3,8-$(COOH)_2$-4,7-$(OH)_2$phen	-
11	[RuL_3]	6,6'-$(COOH)_2$-2,2'-bpy	-
12	[RuL_3] [Ru^{II}, Ru^{III}]	4,4'-$(OMe)_2$-2,2'-bpy	
13	[$RuL_2(H_2O)_2$]	4,4'-$(COOH)_2$-2,2'-biq	-
14	[RuL_2Cl_2]	4,4',5,5'-$(COOH)_4$-2,2'-bpy	-
15	[$RuL_2(CN)_2$]	4,4'-$(COOH)_2$-2,2'-bpy	-
16	[$RuL_2L'(H_2O)$]	4,4'-$(COOH)_2$-2,2'-bpy	4-(COOH)pyridine
17	[$RuL_2L'(H_2O)$]	4,4'-$(COOH)_2$-2,2'-bpy	3,5-$(COOH)_2$pyridine
18	[$RuL_2L'(H_2O)$]	4,4'-$(COOH)_2$-2,2'-bpy	pyridine
19	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	phenylpyridine
20	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	4,4'-$(COOH)_2$-2,2'-biq
21	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	4,4'-$(phenyl)_2$-2,2'-bpy
22	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	$C_{13}H_{27}$-2,2'-bpy
23	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	4,4'-$(Me)_2$-2,2'-bpy
24	[RuL_2L']	2,2'-bpy	1,10-phenanthroline-5,6-dioxime

#	Complex	L	L'
25	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	1,2-bis(2-pyridyl)ethane
26	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	$(Me)_4$-ethylenediamine
27	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	binaphthyl
28	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	3,8-$(COOH)_2$-4,7-$(OH)_2$phen
29	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	dimethylglyoxime
30	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	4,7-$(OH)_2$-1,10-phen
31	[RuL_2L']	4,4'-$(COOH)_2$-2,2'-bpy	2-azopyridylresorcinol
32	[RuL_2L']	4,4'-$(phenyl)_2$-2,2'-bpy	4,4'-$(COOH)_2$-2,2'-bpy
33	[RuL_2L']	4,4'-$(phenyl)_2$-2,2'-bpy	4,7-$(OH)_2$-1,10-phen

The complexes of Examples 1 to 33 are found to be useful as photosensitiser dyes and can be used as such in photovoltaic cells according to the invention.

Example 34

A preferred photovoltaic cell is shown with reference to Figure 1.

A photovoltaic device based on the sensitization of a aluminum-doped titanium dioxide film supported on

conducting glass is fabricated as follows:

A stock solution of organic titanium dioxide precursor is prepared by dissolving 21 mmol of freshly distilled $TiCl_4$ in 10mL of absolute ethanol. $TiCl_4$ in ethanol solution gives titanium alkoxide spontaneously, which on hydrolysis gives TiO_2 The stock solution is then diluted with further absolute ethanol to give two solutions (solution A and solution B having) titanium contents of 25mg/ml (solution A) and 50 mg/ml (solution B). A third solution (C) is prepared from solution B by addition of $AlCl_3$ to yield an aluminium content of 1.25 mg/ml. A conducting glass sheet provided by Asahi Inc. Japan, surface area 10 cm^2 and having a visible light transmittance of at least 85% and a surface resistance smaller than 10 ohms per square cm is used as support for a deposited TiO_2 layer. Prior to use, the glass is cleaned with alcohol. A droplet of solution A is spread over the surface of the conducting glass to produce a thin coating. Subsequently the layer is hydrolyzed at 28°C for 30 minutes in a special chamber where the humidity is kept at 48% of the equilibrium saturation pressure of water. Thereafter, the electrode is heated in air in a tubular oven kept at 450°C, preheating it in the entrance of the oven for 5 minutes followed by 15 minutes of heating in the interior. Three more layers are produced in the same way. Subsequently, 5 thicker layers are deposited by using solution B. The same procedure as for the first layers is applied. Finally, solution C is used to deposit the last two layers containing the aluminum dopant. The heating of the last layer in the tubular oven is extended from 15 to 30 minutes. The total thickness of the titanium dioxide film is between 10 and 20 microns.

Prior to deposition of the dye, the film is subjected to a sintering treatment in highly purified 99.997% argon. A horizontal tubular oven composed of quartz tubes with suitable joints is employed. After insertion of the glass sheet with the TiO_2 film, the tube is twice evacuated and purged with argon. The glass sheet is then heated under argon flux at a flow rate of 2,5L/h and a temperature grandient of 500°C/h up to 550°C at which temperature it maintained for 35 minutes. This treatment produces anatase films with a surface roughness factor of 80-200.

After cooling under a continuous argon flow, the glass sheet is immediately transferred to an alcoholic solution of a chromophore. The chromophore employed is the trimeric ruthenium complex

$$[Ru(L_2)[(CN)_2RuL_2']_2]$$

where L is 2,2'-bipyridyl-4,4'-dicarboxylic acid and L' is 2,2'-bipyridyl. Its concentration in absolute ethanol is $5x10^{-4}$M. Prolonged exposure of the film to the open air prior to dye adsorption is avoided in order to prevent hydroxylation of the TiO_2 surface as the presence of hydroxyl groups at the electrode surface interferes with dye uptake. The adsorption of chromophore from the ethanolic solution is allowed to continue for 30 minutes after which time the glass sheet is withdrawn and washed briefly with absolute ethanol. The TiO_2 layer on the sheet assumed a deep red colour owing to the chromophore coating.

The photocurrent action spectrum was obtained with such a film using a conventional three electrode electrochemical cell containing an ethanolic solution of 0.5M LiI and $3x10^{-3}$M iodine. The incident monochromatic photon to current conversion efficiency (IPCE) was plotted as a function of the excitation wavelength. This was derived from the equation:

$$(1) \qquad \mathrm{IPCE}(\%) = \frac{[(1.24x10^3) \text{ x photocurrentdensity}(\mu A/cm^2)]}{[\text{wavelength}(nm) \text{ x photon flux}(W/m^2)]}$$

From the overlap of the photocurrent action spectrum with solar emission the overall efficiency for the conversion of solar light to electricity η is calculated from the formula

$$(2) \qquad \eta = 12 \text{ x OCV x FF}(\%)$$

where OCV is the open circuit voltage and FF is the fill factor of the photovoltaic cell.

For experimental verification of equation 2, a photovoltaic cell, shown in the draving attached, is constructed, using a dye (4)-loaded TiO_2 (5) film supported on a conducting glass (the working electrode) comprising a transparent conductive tin dioxide layer (6) and a glass substrate (7) as a photoanode. The cell has a sandwich-like configuration, the working electrode (4-7) being separated from the counter electrode (1,2) by a thin layer of electrolyte (3) having a thickness of ca. 20 microns. The electrolyte used is an ethanolic solution of 0.5M LiI and $3x10^{-3}$M iodine. The electrolyte (3) is contained in a small cylindrical reservoir (not shown) attached to the side of the cell from where capillary forces attract it to the inter-electrode space. The counterelectrode comprises the conductive tin dioxide layer (2) deposited on a glass substrate (1) made also of Asahi conducting glass and is placed directly on top of the working electrode. A monomolecular transparent layer of platinum is deposited on to the conducting glass of the counter electrode (1,2) by electroplating from an aqueous hexachloroplatinate solution. The role of the platinum is to enhance the electrochemical reduction of iodine at the counter electrode. The transparent nature of the counterelectrode is an advantage for photovoltaic applications since it allows the harvesting of light from both the forward and the backward direction. Experiments are carried out with a high pressure Xenon lamp equipped with appropriate filters to simulate AM1 solar radiation. The intensity of the light is varied between 50 and 600 Watts per square meter and the open circuit voltage is 660 and 800mV, respectively at these two voltages. The fill factor defined as the maximum electric

power output of the cell divided by the product of open circuit voltage and short circuit current is between 0.7 and 0.75V. A single crystal silicon cell gave an open voltage of 550mV at 600W/M^2 incident light intensity which dropped to below 300mV at 50 W/m2. This clearly shows that the cell of the present invention has a higher open circuit voltage than the silicon solar cell and that the open circuit voltage is less dependent on light intensity than that of the silicon cell. This constitutes a significant advantage for the use of such a cell in indirect sunlight or cloudy weather conditions. The fill factor of the silicon cell is comparable to that of the example. The overall solar light to electricity conversion efficiency of the cell of the example is between 5 and 6%, in agreement with predictions of equation 2.

Examples 35-37 are presented not as embodiments of the invention, but as examples which are useful for understanding the invention.

Example 35

A transparent TiO_2 film from colloidal titanium dioxide particles which are deposited on a conducting glass support and sintered to yield a coherent highly porous semiconducting film that is transparent can be used instead of the TiO_2 layer film in Example 34.

Colloidal titanium oxide particles of approximately 10nm are prepared by hydrolysis of titanium isopropoxide as follows:

125 ml of titanium isopropoxide is added to a solution of 0.1M nitric acid in 750ml of water whilst stirring. A precipitate of amorphous titanium dioxide is formed under these conditions. This is heated to 80°C for approximately 8 hours, stirring vigorously, resulting in peptisation of the precipitate and formation of a clear solution of colloidal anatase. The anatase structure of the titanium dioxide particles is established by Raman spectroscopy. The sol is concentrated by evaporation of the solvent in vacuum at room temperature until a viscous liquid is obtained containing the colloidal particles. At this stage the nonionic surfactant TRITON X-100 (40% weight of TiO_2) is added to reduce cracking of the film when applied to a substrate.

The titanium dioxide films are formed by spin coating the concentrated sol on to a conducting glass substrate. Usually it is sufficient to apply 6 to 10 layers in order to obtain semiconductor membranes of sufficient surface area to give excellent visible light harvesting efficiencies after deposition of a monolayer of the sensitizer.

Low resolution electron microscopy confirms the presence of the three layer structure, the lowest being the glass support followed by the 0.5 micron thick fluorine-doped SnO_2 and the 2.7 micron thick titanium dioxide layer. High resolution electron microscopy reveals the TiO_2 film to be composed of a three dimensional network of interconnected particles having an average size of approximately 16nm. Apparently, significant particle growth occurs during sintering.

The transparent TiO_2 films are tested in conjunction with a sensitizer, Ru L_3 where L is 2,2'bipyridyl-4,4'dicarboxylic acid regenerative cell for the generation of electricity from visible light. The results can be represented where the photocurrent under simulated sunlight (intensity ca 30W/m^2) is plotted as a function of cell voltage. The open circuit voltage under these conditions is 0.52V and the short circuit current 0.381 mA/cm^2. The fill factor is 0.75, yielding an efficiency of 5%. Under the same conditions, a commercial silicon photovoltic cell gave a short circuit current of 1mA and open circuit voltage of 0.4V and a conversion efficiency of 10% which is only a factor of two higher than that obtained with the titanium dioxide membrane.

Example 36

A sheet of conducting glass (ASAHI) of areal resistance ca 10 Ohm/square) having a size of 2x9.6 cm^2 is coated with a colloidal titanium dioxide film according to the procedure of Example 35. A total of 7 layers of TiO_2 colloid are deposited successively by spin coating and the film is subjected each time to calcination at 500°C for 30 minutes. 30% (w/w) of TRITON X 405 surfactant is added in order to avoid cracking of the film.

The final thickness of the titanium dioxide film is 5 microns as determined from the optical interference pattern. It is important to note that the conducting glass sheet after deposition of the TiO_2 remains clear and transparent to visible and near infrared light. The transmission spectrum recorded on a conventional spectrophotometer shows that a fraction of more that 60% of the visible light in the wavelength region between 400 and 900 nm is transmitted through the film. A UV/visible absorption spectrum of the electrode can be obtained. It exhibits a flat feature in the visible due to light absorption and scattering by the conducting glass and the 5 nm thick TiO_2 film. The steeply rising part of the absorption below 400 nm is due to the band gap absorption of the TiO_2.

Immediately before coating with dyestuff, the film is fired for 1 hour at 500°C. The coating of TiO_2 with dyestuff is performed by immersing the glass sheet for 16 hours in an ethanolic solution containing the trimeric

ruthenium complex $RuL_2(CMRuL'_2CN)_2$ where L stands for 2,2-bipyridyl 4,4'-dicarboxylate and L' stands for 2,2'-bipyridyl. After coating, the glass sheet displays an intensive dark red coloration. The optical absorption spectrum measured with a conventional UV/visible spectrophotometer shows the absorbance in the vicinity of 500nm to exceed the value of 2, indicating that in this wavelength range more than 99% of the photons are absorbed by the dyestuff deposited on to the titanium dioxide film. It is important to note that, due to the high concentration of dyestuff, the porous film is capable of harvesting photons over a very broad spectral range extending from 400 to 750 nm.

After dye deposition, the glass sheet is cut into two parts each having a size of ca 9 cm^2. These sheets serve as working electrodes (photo-anodes) in the module whose assembly is described further below.

Transparent counterelectrodes are made of the same type of ASAHI conducting glass as the working electrodes. The counterelectrode was not coated with TiO_2. Instead, the equivalent of 10 monolayers of Pt is electrochemically deposited on to conducting glass. The transparent nature of the counterelectrode is not affected by the deposition of the Pt, its transmission in the visible and near infrared remaining greater that 60%. The Pt acts as an electrocatalyst, enhancing the rate of reduction of the electron transfer mediator, i.e. triiodide, at the counterelectrode. Two ca. 1mm deep and 1.5mm wide and 20mm long indentations are engraved into the surface of the counterelectrode close to the edges of the glass sheets. These serve as a reservoir for the electrolyte.

The counter electrode is placed directly on top of the working electrode to yield a sandwich-type configuration. After filling the reservoirs with electrolyte, the cell was sealed with epoxy resin. The wetting of the space between the two electrodes by the electrolyte occurs spontaneously by capillary action. The electrolyte is a solution of 0.5M tetrapropyl ammonium iodide and 0.02M iodine in ethanol.

Two cells are fabricated in this way, each having a surface area of ca 9cm^2. Subsequently, they are connected in series by electrically contacting the photoanode of one cell to the cathode of the second cell. In this way a module is constructed, having a total surface area of 18 cm 2.

The performance characteristics of this module can be shown, referring to monochromatic light of 520 nm wavelength and an intensity of 0.38W/m2. The short circuit photocurrent of 0.115 mA corresponds to an incident monochromatic photon to current conversion efficiency of 74%. The fill factor is 0.74 and monochromatic power conversion efficiency is 12% at 520nm.

Results can also be produced under natural light conditions. The overall incident light intensity was ca. 3W/m2. Under these conditions, the short circuit photocurrent of the module was 0.76 mA, the fill factor of the cell was 0.73, and the overall conversion efficiency of day light into electrical power was 11%. By comparison, a 1 cm^3 sized commercial silicon cell under the same conditions gave a short circuit photocurrent of 0.17mA, an open circuit voltage of 0.21V, a fill factor of 0.5 and an overall conversion efficiency of 6%. The comparison of these results shows clearly that the performance of the TiO_2 cell under diffuse daylight is superior to that of a conventional silicon device. A final test was performed under direct sunlight in the early morning of the following day. The current output was 60 mA at a solar intensity of ca. 600 W/m2 and the open circuit potential was 1.5V. The fill factor of the cell was reduced to 0.6 due to ohmic losses in the conducting glass, yielding an overall efficiency of 5.6%

Example 37

A preferred photovoltaic cell is shown with reference to Figure 1.

A photovoltaic device based on the sensitization of a transparent TiO_2 film is made from colloidal titanium dioxide particles which are deposited on a conducting glass support and sintered to yield a coherent highly porous semiconducting film.

Colloidal titanium oxide particles of approximately 8 nm are prepared by hydrolysis of titanium isopropoxide as follows:

125ml titanium isopropoxide is added to a solution of 0.1 M nitric acid in 750ml water while stirring. A precipitate of amorphous titanium dioxide is formed under these conditions. This is heated to 80°C for approximately 8 hours, stirring vigorously, resulting in peptisation of the precipitate and formation of a clear solution of colloidal anatase. The propanol formed by the hydrolysis is allowed to evaporate during the heating. The colloidal solution is then autoclaved at 140 to 250°C, preferably 200°C, in a pressure vessel of titanium metal or Teflon for 2 to 20 hours, preferably 16 hours. The resultant sol, containing some precipitate is stirred or shaken to resuspend the precipitate. The resulting sol, minus any precipitate that will not resuspend, is concentrated by evaporation of the solvent in vacuum at room temperature until a viscous liquid is obtained containing the colloidal particles. A typical concentration at this point is 200g/L. At this stage a polyethylene oxide polymer, for example Union Carbide Carbowax 20M or Triton X-405, can be added to increase the thickness of the layer that be deposited without cracks. The polymer is added in amount of 30 to 50, preferably 40, weight percent

TiO_2.

The electrodes for sensitization are formed from the colloidal solution as follows:

A suitable substrate, for example a 3 x 6 cm piece of conductive tin oxide coated glass, for example from Asahi Corp. (but also titanium metal or any flat conductive surface), is placed with the conductive surface up and with suitable spacers, for example 50 to 100 microns, preferably 80 microns thick plastic tape, placed along each edge. A suitable amount of the sol, for example 150 microliters of sol with 200 g/L TiO_2 and 40% Carbowax 20M for the above substrate, is pipetted along one end of the substrate. The sol is spread across the substrate by drawing with a flat edged piece of glass whose ends ride along the spacers. Thus the spacers, the viscosity of the sol, and the concentration of the sol control the amount of TiO_2 deposited. The as-spread film is allowed to dry in room air till visibly dry and preferably for an additional 20 minutes. After drying the electrode is fired at 400 to 500 °C, preferably 450, for a minimum of 20 minutes. In the case of sols autoclaved below 170 °C the spacers of less than 40 microns must be used and the process must be repeated twice to achieve an 8 to 10 microns thick TiO_2 film.

Electrodes of up to 10 cm by 10 cm have been fabricated by this method. The sol can also be applied to substrates by spin coating and dip coating.

The electrode can then be cut to the size desired by normal glass cutting techniques. Immediately before applying the sensitizer the electrode is fired again at 450 to 550, preferably 500 °C for 2 to 12, preferably 6 hours. For some solvent and dye combinations, the surface of the electrode is improved (with respect to electron injection) by firing the electrode 5 to 10, preferably 7 times at 500 °C for 2 to 6 hours with either 10 hours in air or soaking up to 1 hour in water, 0.5M nitric acid or 0.5M HCl, between each firing. The acid solutions are saturated with dissolved TiO_2 before use. After the last firing, immediately after cooling, the electrode is placed in the sensitizer solution. Preferably, an ethanolic solution containing the trimeric ruthenium complex $RuL_2(CNRuL'_2CN)_2$ where L stands for 2,2-bipyridyl 4,4'-dicarboxylate and L' stands for 2,2'-bipyridyl, but also equally an ethanolic solution of RuL_2NCS_2 or $RuL_1L'_1H_2O$ where L' stands for 2,6-bis(N-methylbenzimidazol-2'-yl)pyridine. Depending on the sensitizer, between 4 and 24 hours are required for the electrode to gain full color. Full color can be estimated by eye or by taking visible light transmittance spectra of the dye at various times.

After removal from the dye solution, the electrode is made into a photovoltaic cell as follows:

Transparent counterelectrodes are made of the same type of ASAHI conducting glass as the working electrodes. The counterelectrode is not coated with TiO_2. Instead, the equivalent of 10 monolayers of Pt is electrochemically deposited onto conducting glass. The transparent nature of the counterelectrode is not affected by the deposition of the Pt, its transmission in the visible and near infrared remains greater that 60%. The Pt acts as an electrocatalyst enhancing the rate of reduction of the electron transfer mediator, i.e. triiodide, at the counterelectrode. Alternatively, a thin titanium sheet, which may be porous coated as above with Pt, may be used as a counterelectrode. In the case of a porous sheet, another sheet of impervious material is required behind the counterelectrode, such as plastic, glass or metal.

A reservoir is provided for the electrolyte by engraving two ca 1mm deep and 1.5mm wide and 20mm long clefts into the surface of the counterelectrode close to the edges of the glass sheet. The reservoir can also be added external to the glass sheets or be behind the counterelectrode in the case of porous counterelectrode.

The countereletrode is placed directly on top of the working electrode to yield a sandwich type configuration. The reservoirs are filled with electrolyte solution, selected from the list above but preferably 85% by weight ethylene carbonate, 15% propylene carbonate 0.5M potassium iodide and 40mM iodine. An amount of LiI or tetraalkylammonium iodide can be present (preferably 20mM), depending on the voltage desired. The cell is sealed around the edge with a sealant compatible with the solvent chosen and bonded closed with an adhesive. The sealant and the adhesive may be the same material, for example silicon adhesive in the case of the alcohol solvents, or for example, polyethylene and epoxy resin (or mechanical closure) in the case of ethylene carbonate. The wetting of the space between the two electrodes by the electrolyte injected into the reservoirs occurs spontaneously by capillary action.

Photovoltaic cells of the type described in the preceding paragraphs have produced up to 12mA/cm^2 short circuit current and up to 830mV open circuit voltage under simulated sunlight of 80mW/cm^2. The most efficient combination has been 9.6mA/cm^2 and 620 mV with a fill factor or 51%, thus an energy conversion efficiency of 3.8%. Fill factors above 60% have been measured.

The complexes of the other examples of Examples 1 to 33 can be used in place of the ruthenium complexes of Examples 34 to 37 in the photovoltaic cell.

Claims

1. A solar-light-responsive photovoltaic cell comprising a first electrode (4, 5, 6, 7) including
   i) a light transmitting electrically conductive layer (6) deposited on a glass plate (7) or a transparent polymer sheet;
   ii) at least one porous high surface area titanium dioxide layer (5) applied to said light transmitting electrically conductive layer (6),
   iii) a dopant applied to at least the outermost titanium dioxide layer, said dopant being selected from a divalent metal ion, trivalent metal ion and boron; and
   iv) a photosensitizer (4) applied to the dopant-containing TiO_2 layer (5), said photosensitizer being attached to the TiO_2 layer by means of interlocking groups, said interlocking groups being selected from carboxylate groups, cyano groups, phosphate groups and chelating groups with π-conducting character selected from oximes, dioximes, hydroxy quinolines, salicylates and α -keto-enolates.

2. A solar-light-responsive photovoltaic cell according to claim 1, further comprising
   i) a second electrode (1, 2), at least one of the first and second electrodes being transparent and having a visible light transmittance of at least 60%, the electrodes (1, 2) and (4, 5, 5, 7) being arranged so as to define a receptacle between them, in which receptacle an electrolyte (3) containing a redox system is located, and
   ii) means for permitting the output of an electrical current generated by the cell.

3. A photovoltaic cell comprising
   i) an electrically conductive first plate (6, 7) on which a multilayer TiO_2 film (5) having a thickness of 0.1-50 μm is coated, said TiO_2 film being coated with a transition metal complex photosensitizer attached to the TiO_2 layer by means of interlocking groups, said interlocking groups being selected from carboxylate groups, cyano groups, phosphate groups and chelating groups with π- conducting character selected from oximes, dioximes, hydroxy quinolines, salicylates and α-keto-enolates, at least the outermost layer of the TiO_2 film being doped with a dopant selected from a divalent metal ion, trivalent metal ion and boron,
   ii) and a conductive second plate separated from the first plate by a thin layer of electrolyte (3), whereby the visible light transmittance of at least one of the plates is at least 60% and only the first plate has a TiO_2 coating.

4. A photovoltaic cell according to any one of the preceding claims in which the interlocking groups are selected from carboxylates and cyano groups.

5. A photovolataic cell according to claim 1 in which the photosensitizer is a ruthenium, osmium or iron complex or a combination of two or three transition metals in one supermolecular complex.

6. A photovoltaic cell, according to any one of the preceding claims in which the photosensitizer is a transition metal complex, the ligands being bidentate or tridentate or polydentate polypyridyl compounds, which may be unsubstituted or substituted.

7. A photovoltaic cell, according to claim 5 in which the photosensitizer is selected from ruthenium or osmium complexes.

8. A photovoltaic cell according to any one of the preceding claims in which the photosensitizer is selected from a compound of the formula (1) to (10)

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(CN)(L^c)(L^d))_2] \qquad (1)$$

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN)M(CN)(L^c)(L^d))_2] \qquad (2)$$

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN))_2M(L^c)(L^d)] \qquad (3)$$

$$[(L^a)(L^b)(X)M\ \mu\text{-}(NC)M(CN)(L^c)(L^d)] \qquad (4)$$

$$[M(L^a)(L^b)(X)_2] \qquad (5)$$

$$[M(L^a)(L^b)(L^c)] \qquad (6)$$

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^g))_2] \qquad (7)$$

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^d)\ \mu\text{-}(CN)M(L^c)(L^g))_2] \qquad (8)$$

$$[M(L^a)(L^g)\ \mu\text{-}(NC)M(L^g)(L^b)] \qquad (9)$$

$$[M(L^a)(L^g)(X)] \qquad (10)$$

in which each M is independently selected from ruthenium, osmium and iron;

μ-(CN) or μ-(NC) indicates that the cyano group bridges two metal atoms;
each L^a, L^b, L^c and L^d independently is selected from 2,2'-bipyridyl, unsubstituted or substituted by one or two COOH groups; 2,2' bipyridyl substituted by one or two groups selected from C_{1-16}alkyl, C_{1-16}alkoxy and diphenyl; 2,2'-biquinoline unsubstituted or substituted by one or two carboxy; groups; phenanthroline, unsubstituted or substituted by one or two carboxy groups and/or one or two hydroxy groups, and/or one or two dioxime groups; bathophenanthroline disulfonic acid; diaza-hydroxy- carboxyl-triphenylene; carboxy pyridine;phenyl pyridine; 2,2'-Bis(diphenylphosphino) 1,1'- binaphthalene; (pyridyl azo) resorcinol; bis (2-pyridyl) C_{1-4}alkane; tetra C_{1-4}alkyl ethylene diamine;and di-C_{1-4}alkyl glyoxime;
L^g is selected from terpyridyl, unsubstituted or substituted by phenyl, which phenyl group is unsubstituted or substituted by COOH and dicarboxy-pyridine, preferably 2,6-dicarboxy-pyridine;
each X independently is halogen, H_2O, CN, amine (primary or secondary alkylamine) and/or pyridine.

9. A photovoltaic cell according to claim 2 wherein an electrode comprising a transparent TiO_2 (5) layer on a glass support (7) is provided.

Patentansprüche

1. Eine auf Solarlicht ansprechende photovoltaische Zelle umfaßt eine erste Elektrode (4, 5, 6, 7), die
   i) eine lichttransmittierende elektrisch leitende Schicht (6), die auf eine Glasplatte (7) oder eine transparente dünne Polymerplatte aufgetragen ist;
   ii) wenigstens eine poröse Titandioxidschicht (5) mit hohem Oberflächenbereich, welche auf die besagte lichttransmittierende elektrisch leitende Schicht (6) aufgetragen ist;
   iii) einen Dotierstoff, der auf wenigstens die äußerste Titandioxidschicht aufgetragen ist, wobei der Dotierstoff ausgewählt wird aus einem zweiwertigen Metallion, dreiwertigen Metallionen und Bor; und
   iv) einem Photosensibilisator (4) aufweist, der auf die dotierstoffhaltige TiO_2-Schicht (5) aufgetragen ist, wobei der Photosensibilisator an die TiO_2-Schicht mit Kupplungsgruppen gebunden ist, welche Kupplungsgruppen ausgewählt werden aus Carboxylat-Gruppen, Cyan-Gruppen, Phosphat-Gruppen und Chelat-Gruppen mit π-leitendem Charakter, ausgewählt aus Oximen, Dioximen, Hydroxychinolinen, Salicylaten und α-Keto-Enolaten.

2. Eine auf Solarlicht ansprechende photovoltaische Zelle nach Anspruch 1, welche außerdem aufweist
   i) eine zweite Elektrode (1, 2), wobei wenigstens eine der ersten oder der zweiten Elektroden transparent ist und einen Durchlaßgrad für sichtbares Licht von wenigstens 60% aufweist, wobei die Elektroden (1, 2) und (4, 5, 5, 7) derart angeordnet sind, daß sie dazwischen eine Aufnahme bilden, in welcher Aufnahme ein Elektrolyt (6), der ein Redox-System aufweist, angeordnet ist, und
   ii) eine Einrichtung zur Ermöglichung der Abgabe des elektrischen Stromes, der von der Zelle erzeugt wird.

3. Eine photovoltaische Zelle, welche umfaßt
   i) eine elektrisch leitende erste Platte (6, 7), die mit einem Mehrschicht-TiO_2-Film (5) mit einer Dicke von 0,1 bis 50 μm beschichtet ist, wobei der besagte TiO_2-Film mit einem Übergangsmetallkomplexphotosensibilisator beschichtet ist, welcher an die TiO_2-Schicht mit Kupplungsgruppen gebunden ist, wobei die Kupplungsgruppen ausgewählt werden aus Carboxylat-Gruppen, Cyan-Gruppen, Phosphat-Gruppen und Chelat-Gruppen mit π-leitendem Charakter, ausgewählt aus Oximen, Dioximen, Hydrochinolinen, Salicylaten und α-Keto-Enolaten, wobei wenigstens die äußerste Schicht des TiO_2-Films mit einem Dotierstoff dotiert ist, der aus einem zweiwertigen Metallion, dreiwertigen Metallion und Bor ausgewählt ist,
   ii) und eine leitende zweite Platte, die von der ersten Platte durch eine dünne Schicht eines Elektrolyten (3) getrennt ist, wobei der Durchlaßgrad wenigstens einer der Platten für sichtbares Licht wenigstens 60% beträgt und nur die erste Platte eine TiO_2-Beschichtung aufweist.

4. Eine photovoltaische Zelle nach einem der vorstehenden Ansprüche, bei der die Kupplungsgruppen aus Carboxylaten und Cyan-Gruppen ausgewählt sind.

5. Eine photovoltaische Zelle nach Anspruch 1, bei der der Photosensibilisator ein Ruthenium-, Osmium- oder Eisenkomplex oder eine Kombination von zwei oder drei Übergangsmetallen in einem Supermolekularkomplex ist.

6. Eine photovoltaische Zelle nach einem der vorstehenden Ansprüche, bei der der Photosenisibilisator ein Übergangsmetallkomplex ist, wobei die Liganden zweizähnige oder dreizähnige oder vielzähnige Polypyridylverbindungen sind, die unsubstituiert oder substituiert sein können.

7. Eine photovoltaische Zelle nach Anspruch 5, bei der der Photosensibilisator ausgewählt wird aus Ruthenium- oder Osmiumkomplexen.

8. Eine photovoltaische Zelle nach einem der vorstehenden Ansprüche, bei der der Photosensibilisator ausgewählt wird aus einer Verbindung der Formel (1 bis 10)

$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(CN)(L^c)(L^d))_2] \qquad (1)$$
$$[M(L^a)(L^b)\ (\mu(NC)M(L^c)(L^d)\mu\text{-}(CN)M(CN)(L^c)(L^d))_2] \qquad (2)$$
$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN)_2M(L^c)(L^d)] \qquad (3)$$
$$[(L^a)(L^b)(X)M\ \mu\text{-}(NC)M(CN)(L^c)(L^d)] \qquad (4)$$
$$[M(L^a)(L^b)(X)_2] \qquad (5)$$
$$[M(L^a)(L^b)(L^c)] \qquad (6)$$
$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^g))_2] \qquad (7)$$
$$[M(L^a)(L^b)\ (\mu\text{-}(NC)M(L^c)(L^d)\ \mu\text{-}(CN)M(L^c)(L^g))_2] \qquad (8)$$
$$[M(L^a)(L^g)\ \mu\text{-}(NC)M(L^g)(L^b)] \qquad (9)$$
$$[M(L^a)(L^g)(X)] \qquad (10)$$

worin M jeweils unabhängig ausgewählt wird aus Ruthenium, Osmium und Eisen; μ-(CN) oder μ-(NC) angibt, daß die Cyan-Gruppe zwei Metallatome überbrückt;
L^a, L^b, L^c und L^d jeweils unabhängig ausgewählt werden aus 2,2-Bipyridyl, unsubstituiert oder durch ein oder zwei COOH-Gruppen substituiert; 2,2'-Bipyridyl, substituiert durch eine oder zwei Gruppen, ausgewählt aus C_{1-18}-Alkyl., C_{1-18}-Alkoxy und Diphenyl; 2,2'-Bichinolin, unsubstituiert durch eine oder zwei Carboxy-Gruppen; Phenanthrolin, unsubstituiert oder substituiert durch eine oder zwei Carboxy-Gruppen und/oder eine oder zwei Hydroxy-Gruppen und/oder eine oder zwei Dioxim-Gruppen; Bathophenanthrolindisulphonsäure, Diazahydroxycarboxyltriphenylen; Carboxypyridin; Phenylpyridin; 2,2'-Bis(diphenylphosphin)1,1'-binaphthalin; (Pyridylazo)resorcin; Bis(2-pyridyl)C_{1-4}-Alkan; Tetra-C_{1-4}-Alkylethylendiamin und Di-C_{1-4}-Alkyldioxim;
L^g ausgewählt ist aus Terpyridyl, unsubstituiert oder substituiert durch Phenyl, wobei die Phenyl-Gruppe unsubstituiert oder durch COOH und Dicarboxy-pyridin, vorzugsweise 2,6-Dicarboxypyridin, substituiert ist;
X jeweils unabhängig ein Halogen, H_2O, CN, Amin (primäres oder sekundäres Alkylamin) und/oder Pyridin ist.

9. Eine photovoltaische Zelle nach Anspruch 2, wobei eine Elektrode vorgesehen ist, die eine transparente TiO_2-Schicht (5) auf einem Glasträger (7) umfaßt.

Revendications

1. Cellule photovoltaïque sensible à la lumière solaire, comprenant une première électrode (4, 5, 6, 7) incluant :
   i) une couche électriquement conductrice (6), transmettant la lumière, déposée sur une plaque de verre (7) ou une feuille transparente de polymère;
   ii) au moins une couche (5) poreuse de bioxyde de titane ayant une valeur élevée de surface effective, appliquée sur ladite couche électriquement conductrice (6) transmettant la lumière;
   iii) un dopant appliqué sur au moins la couche extérieure extrême de bioxyde de titane, ledit dopant étant choisi parmi un ion de métal divalent, un ion de métal trivalent et le bore; et,
   iv) un photosensibilisateur (4) appliqué sur la couche (5) de TiO_2 contenant du dopant, ledit photosensibilisateur étant fixé sur la couche de TiO_2 au moyen de groupes de liaison, lesdits groupes de liaison étant choisis parmi les groupes carboxylate, les groupes cyano, les groupes phosphate et les groupes chélatants ayant un caractère de conduction π choisis parmi les oximes, les dioximes, les hydroxy-quinoléines, les salicylates et les α-kéto-énolates.

2. Cellule photovoltaïque selon la revendication 1, comprenant en outre :
   i) une deuxième électrode (1, 2), au moins l'une des première et deuxième électrodes étant transparente et ayant une transmittance de la lumière visible au moins égale à 60 %, les électrodes (1, 2) et

(4, 5, 5, 7) étant disposées de façon à définir un récipient entre elles, un électrolyte (3) contenant un système redox étant placé dans ce récipient, et
ii) des moyens pour permettre le débit d'un courant électrique engendré par la cellule.

3. Cellule photovoltaïque comprenant:
i) une première plaque électriquement conductrice (6, 7) sur laquelle est appliquée une pellicule (5) de revêtement à couches multiples en TiO_2 ayant une épaisseur de 0,1 - 50 μm, ladite pellicule de TiO_2 étant revêtue d'un photosensibilisateur en complexe de métal de transition, fixé sur la couche de TiO_2 au moyen de groupes de liaison, les groupes de liaison étant choisis parmi les groupes carboxylate, les groupes cyano, les groupes phosphate et les groupes chélatants ayant un caractère de conduction π choisis parmi les oximes, les dioximes, les hydroxy-quinoléines, les salicylates et les α-kéto-énolates, au moins la couche extérieure extrême de la pellicule de TiO_2 étant dopée par un dopant choisi parmi un ion de métal divalent, un ion de métal trivalent et le bore,
ii) et une deuxième plaque conductrice séparée de la première plaque par une couche mince d'électrolyte (3), la transmittance en lumière visible d'au moins l'une des plaques étant au moins de 60 % et seule la première plaque ayant un revêtement de TiO_2.

4. Cellule photovoltaïque selon l'une quelconque des revendications précédentes dans laquelle les groupes de liaison sont choisis parmi les groupes carboxylates et cyano.

5. Cellule photovoltaïque selon la revendication 1, dans laquelle le photosensibilisateur est un complexe de ruthénium, osmium ou fer ou une combinaison de deux ou trois métaux de transition dans un complexe supermoléculaire.

6. Cellule photovoltaïque selon l'une quelconque desrevendications précédentes dans laquelle le photosensibilisateur est un complexe de métal de transition, les ligands étant des composés bidentates ou tridentates ou polydentates polypyridyles qui peuvent être non substitués ou substitués.

7. Cellule photovoltaïque selon la revendication 5, dans laquelle le photosensibilisateur est choisi parmi les complexes de ruthénium ou d'osmium.

8. Cellule photovoltaïque selon l'une quelconque des revendications précédentes dans laquelle le photosensibilisateur est choisi parmi les composés de formules (1) à (10)

$$[M(L^a)(L^b)(\mu\text{-}(NC)M(CN)(L^c)(L^d))_2] \qquad (1)$$
$$[M(L^a)(L^b)(\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN)M(CN)(L^c)(L^d))_2] \qquad (2)$$
$$[M(L^a)(L^b)(\mu\text{-}(NC)M(L^c)(L^d)\mu\text{-}(CN))_2M(L^c)(L^d)] \qquad (3)$$
$$[(L^a)(L^b)(X)M\ \mu\text{-}(NC)M(CN)(L^c)(L^d)] \qquad (4)$$
$$[M(L^a)(L^b)(X)_2] \qquad (5)$$
$$[M(L^a)(L^b)(L^c)] \qquad (6)$$
$$[M(L^a)(L^b)(\mu\text{-}(NC)M(L^c)(L^g))_2] \qquad (7)$$
$$[M(L^a)(L^b)(\mu\text{-}(NC)M(L^c)(L^d)\ \mu\text{-}(CN)M(L^c)(L^g))_2] \qquad (8)$$
$$[M(L^a)(L^g)\ \mu\text{-}(NC)M(L^g)(L^b)] \qquad (9)$$
$$[M(L^a)(L^g)(X)] \qquad (10)$$

dans lesquelles chaque M est indépendamment choisi parmi le ruthénium, l'osmium et le fer; μ-(CN) ou μ-(NC) indique que le groupe cyano forme un pont entre deux atomes de métal;
chaque L^a, L^b, L^c et L^d est indépendamment choisi parmi 2,2'-bipyridyle, non substitué ou substitué par un ou deux groupes COOH; 2,2'-bipyridyle substitué par un ou deux groupes choisi parmi C_{1-16} alkyle, C_{1-16} alcoxy et diphényle; 2,2'-biquinoléine non substituée ou substituée par un ou deux groupes carboxy; phénanthroline non substituée ou substituée par un ou deux groupes carboxy et/ou un ou deux groupes hydroxy, et/ou un ou deux groupes dioxime; acide bathophénanthroline disulfonique; diazahydroxy-carboxyl-triphénylène; carboxy pyridine; phényl pyridine; 2,2'-bis (diphénylphosphino) 1,1'-binaphtalène; (pyridyl azo) résorcinol; bis (2-pyridyl) C_{1-4} alcane; tétra C_{1-4} alkyl éthylène diamine; et di-C_{1-4} alkyl glyoxime;
L^g est choisi parmi terpyridyle, non substitué ou substitué par phényle, ledit phényle étant non substitué ou substitué par COOH et dicarboxy-pyridine, de préférence 2,6-dicarboxy-pyridine;
chaque X, indépendamment, étant halogène, H_2O, CN, amine (alkylamine primaire ou secondaire) et/ou pyridine.

9. Cellule photovoltaïque selon la revendication 2, munie d'une électrode comprenant une couche transparente en TiO_2 (5) sur un support en verre (7).

FIG. 1.